II.D.4 Hydrogen Reactor Development and Design for Photofermentation and Photolytic Processes

Daniel M. Blake (Primary Contact) and Cheryl Kennedy
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401
Phone: (303) 384-7701; Fax: (303) 384-6363; E-mail: Daniel_blake@nrel.gov

DOE Technology Development Manager: Roxanne Danz
Phone: (202) 586-7260; Fax: (202) 586-9811; E-mail: Roxanne.Danz@ee.doe.gov

Objectives

- Identify three transparent material candidates.
- Initiate accelerated and outdoor weathering tests.
- Measure key properties for the photolytic reactor application.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- L. Systems Engineering
- N. Materials and System Engineering

Approach

- Survey transparent materials for use as the cover for photolytic water splitting reactors.
- Identify promising candidates based on existing durability information and new materials from vendors.
- Evaluate material durability using accelerated and outdoor weathering tests.
- Measure key physical and mechanical properties as a function of time in the durability tests.
- Identify materials properties that require modification or improvement to meet the system requirements.
- Build on 25 years of experience in evaluation of materials for solar applications at the National Renewable Energy Laboratory (NREL).

Accomplishments

- Identified baseline operating requirements for the photolytic water splitting processes.
- Mined existing data on performance of polymers in solar and outdoor applications.
- Initiated accelerated and outdoor testing of three polymers - polycarbonate with protective acrylic layer attached with adhesive, fluorinated polymer, and polycarbonate with a Tefzel™ protective layer (we are working with a vendor to obtain polycarbonate with a co-extruded protective layer).
- Establishing oxygen and hydrogen permeability test capability to evaluate materials.

Future Directions

- Measure time-zero properties of the polymer samples.
- Continue accelerated and outdoor exposures for the polymers.

- Begin measuring properties of samples as a function of exposure time.
- Identify new solar hydrogen reactor configurations for photobiological and photoelectrochemical solar reactor systems.
- Provide reactor design, expected performance, and materials of construction for systems analysis of promising solar hydrogen production reactor concepts.

Introduction

Hydrogen from natural gas and coal will be part of the transition to a hydrogen economy. However, the ultimate goal of the Hydrogen Program is the renewable production of hydrogen from water using wind, sunlight, or other sources of low-cost and abundant energy. A few of the projects being funded by the DOE Hydrogen Program include algal hydrogen production from sunlight, photoelectrochemical hydrogen production from sunlight, dark-phase fermentative hydrogen production, and photo-fermentation of hydrogen from alcohols and waste acids. All of these processes have promise and have been demonstrated at the laboratory scale, but in many cases these projects lack information on the eventual reactor designs and system layouts that will make them commercially feasible. It is too early to start looking at the final system designs, but it is not too early to determine if there are materials or engineering issues that may affect the path of ongoing research. This task addresses reactor, materials and system design issues identified in Technical Tasks 12, 14, 16, and 17 of the draft Multi-Year Research, Development and Demonstration Plan.

Capturing energy from the sun for the production of hydrogen creates challenges in materials of construction. Important materials characteristics are cost and the ability to transmit or concentrate light, but these are general concepts. Specific characteristics of the materials are also important, such as gas permeability rates, which specific wavelengths of light are transmitted, ultraviolet (UV) stability, chemical stability, biocompatibility, etc. Many of these characteristics have been measured for plastics and glass. However, solar applications and hydrogen production in particular have unique requirements and tight economic constraints. It is necessary to evaluate durability and performance with the solar hydrogen requirements as targets.

Approach

This was the first year for this activity. We reviewed the literature for materials used in solar applications, talked with experts in the field, and mined data from ongoing work on materials durability from solar programs at NREL. The results were combined with the performance requirements established in consultation with researchers working on the solar hydrogen production technologies. This resulted in identification of the most promising classes of transparent polymeric materials. Some of these materials were already being tested for other programs, and vendors were contacted for information on new formulations and configurations. Existing methods for evaluation of the key performance properties were cataloged, and new methods, mainly those for oxygen and hydrogen permeability, were identified. By the end of FY 2004, baseline properties for the as-received material samples will be measured, and methods will be in place for the periodic measurement of the properties as samples are monitored during the accelerated and outdoor exposure periods. The results of the testing will allow long-term performance to be quantified and will provide guidance for areas where improvements in material properties will be required.

Results

We have identified three types of polymers that have good outdoor performance characteristics. These are polycarbonate, polyacrylic, and fluorocarbon polymers. A fourth type of polymer, polyester, has many positive characteristics, but outdoor durability is not yet demonstrated to be as good as for the other three. The performance of polymers for specific uses can be improved by engineering to improve specific properties. This results in a wide range of formulations and constructions within a given type of polymer. The formulations are usually developed by the suppliers in response to customer demands. NREL has

Figure 1. Durability Test Options Available to the Task

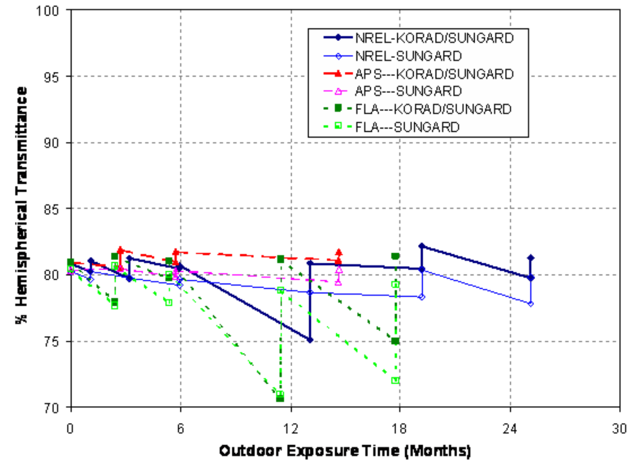

Figure 2. Outdoor Weathering for Polycarbonate Samples

contacts with a number of suppliers of polymers to markets that require outdoor service. This provides access to samples for testing.

During the first three quarters of FY 2004, we have identified the most important operating requirements for the materials of construction for solar photoelectrochemical and photobiological hydrogen production reactors. These are summarized in Table 1. Key properties are optical transparency (for the cover), permeation rates for hydrogen and oxygen, and the effect of outdoor exposure on all properties and service life. The cover is most affected by outdoor exposure, potentially has the greatest physical area, and is the light-gathering element. For these reasons, we have initiated work on weathering and properties for appropriate materials for this component.

A full range of accelerated and outdoor exposure capability is available for the project. These are illustrated in Figure 1. Samples of relevant materials were already being tested for other programs at the start of this project. The dependence of optical performance on polycarbonate formulations under outdoor exposure is shown in Figure 2.

We are in the process of reestablishing in-house capability for measuring oxygen permeation rates. For hydrogen permeation measurements, we are negotiating with a local company that has long experience with hydrogen permeation measurements for materials that are used for containment of radioactive wastes by DOE. NREL has capability for the optical, mechanical, and physical characterization of polymer, glass, thin film, and metal samples.

Table 1. Photolytic Reactor Materials Specifications

Property	Algal Hydrogen	PEC	Photo-fermentation
pH Lower Limit	6.5 (Biological limit)	0-7 (Acidic System, 3 M H_2SO_4)	6.5
pH Average/ Design	7-9 optimum	0-2 (3M H_2SO_4) or 10-14 (1M KOH), Acidic PEC Material More Stable	7 (higher pH give better H_2 yield)
pH Upper Limit	8.2 (biological limit)	7-14 (Alkaline System, 1M KOH)	7.5-8.0
Wavelength - Lower	>320 nm (shorter causes cell damage)	350 nm or 3.0 eV (412 nm=3.0 eV)	400 nm
Wavelength - Optimum	400-700 nm (visible/ PAR light, peaks for blue and red)	500 nm, Entire range works equally well	Visible Light
Wavelength - Upper	700 nm (over 700 nm OK, but not useful to organism)	Minimum 1.8 eV (689 nm=1.8 eV)	900 nm
Light Intensity - Lower	Uses all available light at low intensities.	0.1 sun	Uses all available light at low intensities.
Light Intensity - Optimum	Depends on O_2 inhibition, 40 uE/m^2 s PAR current optimum, 80 uE/m^2 s full spectrum	1 sun, Uses all available light.	Depends on saturation limit for organism.
Light Intensity - Upper	0.05-0.10 suns current saturation, multiple suns causes problems	10 suns	Depends on saturation limit for organism.
Pressure - Lower Limit (Vacuum?)	No need for vacuum, but acceptable.	a few psig	
Pressure - Design	1 atm currently demonstrated	1 bar	
Pressure - Upper Limit	As high as practical, 100 psig?	As high as practical, 100 psig?	As high as practical, 100 psig?

Table 1. Photolytic Reactor Materials Specifications

Property	Algal Hydrogen	PEC	Photo-fermentation
Temperature - Lower Limit	27°C (biological limit)	- 20°C (limited by freezing point of electrolyte solution)	25°C
Temperature - Optimum	30°C optimum	25°C	35°C
Temperature - Upper Limit	32°C (biological limit)	80°C (limited by water vapor pressure)	38°C
Partial Pressure of H_2 in Headspace	100% H_2 at operating pressure in sulfur-deprived system	100 % H_2 at operating pressure (on one side)	May be as high as 90% H_2 with CO_2.
Partial Pressure of O_2 in Headspace	Low. Less than 10 ppm currently. A few % in future. Explosive limits in oxygen tolerant.	100% O_2 at operating pressure (on other side)	None. Anaerobic organism.
Potential VOCs in headspace	Less than 1% organic acids (formate, acetate, ethanol) in solution.	None.	Organic acid substrates (propionate & buterate).
Potential for biofilm growth	Yes. Glass & Teflon resistant to growth.	Low likelihood. High/low pH.	Yes.
Cleaning Method/ Chemicals	Bleach, caustic or acid.	High/low pH is cleaning solution.	Bleach, caustic or acid.
Maximum H_2 Production per m2	Limited by light absorption/antennae size.	3.3 L/m^2/d or 0.56L/m^2/hr for 6 hour days	Limited by light absorption/ antennae size.

Conclusions

- Some acrylics have good outdoor durability but are brittle and subject to hail damage.
- Polycarbonates are tough but "yellow" and crack outdoors.
- Polyester formulations have not yet proven durable outdoors.
- Low-cost polymers like polyethylene, polystyrene, and polypropylene have poor outdoor performance.
- Polymer formulations for outdoor applications are available that overcome the above shortcomings to varying degrees.
- No show-stoppers have been identified at this early stage of work.

FY 2004 Publications/Presentations

1. Poster presentation at the Hydrogen, Fuel Cells & Infrastructure Technologies Program Review Meeting, Philadelphia, PA, May 2004.